

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



2

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08K 5/3492, C08L 63/00	A1	(11) International Publication Number: WO 97/08235
		(43) International Publication Date: 6 March 1997 (06.03.97)
(21) International Application Number: PCT/US96/13831 (22) International Filing Date: 28 August 1996 (28.08.96) (30) Priority Data: 60/002,950 30 August 1995 (30.08.95) US (71) Applicant: CYTEC TECHNOLOGY CORP. [US/US]; Suite 952, 1105 North Market Street, Wilmington, DE 19801 (US). (72) Inventors: GUPTA, Ram, Baboo; 2986 Marion Avenue #A4, Bronx, NY 10458 (US). WU, Kuang, Jong; 55 Honeysuckle Hill Lane, Easton, CT 06612 (US). (74) Agent: LERMAN, Bart, E.; Cytec Industries Inc., 1937 West Main Street, P.O. Box 60, Stamford, CT 06904-0060 (US).		(81) Designated States: BR, CA, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: COMPOSITIONS CONTAINING 1,3,5-TRIAZINE CARBAMATES AND EPOXY COMPOUNDS		
(57) Abstract Curable compositions which include a 1,3,5-triazine carbamate cross-linker and a polyfunctional epoxy resin as well as their uses in coatings are disclosed. The present curable compositions may additionally contain a co-cross-linker and/or a polyfunctional hydroxy group containing material. By using the curable compositions of the present invention, a significant reduction in the formaldehyde emission levels relative to aminoplast resin based coatings can be achieved without loss of the ultimate film properties. The curable compositions of the present invention are usable in coatings, particularly in coatings of the type commonly used in original equipment manufacture and general industrial coatings applications.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Larvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

**COMPOSITIONS CONTAINING 1,3,5-TRIAZINE CARBAMATES
AND EPOXY COMPOUNDS**

BACKGROUND OF THE INVENTION

5

Field of the Invention

The present invention relates generally to a curable composition containing a 1,3,5-triazine carbamate crosslinker and a polyfunctional epoxy compound, preferably suitable for use in coatings. The invention also relates to a method of preparing such coatings and to articles coated therewith.

10

Description of Related Art

Traditional industrial coatings have for years been based in significant part on backbone resins having active hydrogen groups crosslinked with various derivatives of amino-1,3,5-triazines. Most notable among the amino-1,3,5-triazine derivatives are the aminoplasts such as the alkoxymethyl derivatives of melamine and guanamines which, while providing excellent results in a number of aspects, have the disadvantage of releasing formaldehyde as a volatile by-product under curing conditions.

15

Despite the excellent films which can be achieved with aminoplast crosslinked systems, the coatings industry is under great pressure to reduce the environmentally undesirable emission of formaldehyde. As a result, it has long been a desire of industry to find acceptable alternative crosslinkers and coatings systems which do not emit formaldehyde upon cure.

20

One approach by industry to avoid formaldehyde emissions has been the use of epoxy group-containing compounds cured with, for example, polyamine and/or polyacid crosslinking agents. While such epoxy-based systems are in general formaldehyde free and can produce films and other crosslinked objects with a number of desirable physical characteristics, such systems do suffer from several disadvantages including, for example, toxicity of the crosslinkers (particularly the polyamines), poor light stability and excessive yellowing of the cured films upon exposure to the elements, and difficulty in formulating stable one-can systems due to the extreme reactivity of the epoxy group with the amino and carboxyl functional groups of the crosslinking agents.

25

30

It would, therefore, be highly desirable to provide a curable composition based upon an epoxy-functional resin which retains the many advantages of epoxy-based systems but, at the same time, overcomes at least in part the toxicity, stability and formulation problems mentioned above.

5

SUMMARY OF THE INVENTION

In accordance with the present invention, such an advantageous epoxy-based curable composition has been found which comprises, in its overall concept:

- 10 (1) a resin component comprising a polyfunctional epoxy compound, and
 (2) a crosslinker component comprising a 1,3,5-triazine carbamate.

These curable compositions in accordance with the present invention may be utilized in a wide variety of fields. A particularly preferred end use is as a one- or two-component sprayable coating for elevated temperature cure applications such as, for example,
15 automotive OEM clearcoats and coil coatings.

As compared with traditional aminoplast crosslinked systems, the curable compositions of the present invention can be formulated to significantly reduce or even eliminate formaldehyde emissions on cure while retaining many of the advantageous physical properties of aminoplast crosslinked systems. The present systems also retain
20 many of the advantageous physical properties of epoxy-based systems, while significantly improving the resistance and formulating disadvantages inherent to such systems. Particularly, the curable compositions of the present invention provide crosslinked films or objects possessing advantageous acid etch resistance, chemical resistance, hydrolysis resistance and durability, are relatively low in toxicity, can be formulated as stable one-can
25 systems, as liquid and powder systems, and can be formulated for lower temperature cure (100°C to 140°C) applications.

These and other features and advantages of the present invention will be more readily understood by those of ordinary skill in the art from a reading of the following detailed description.

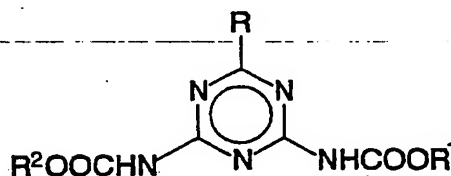
30

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTSThe Crosslinker Component

As indicated above, the crosslinkers component comprises a 1,3,5-triazine carbamate. In addition, the crosslinker component may optionally comprise a co-crosslinker such as an aminoplast resin (e.g., an alkylated melamine-formaldehyde condensate), blocked and unblocked polyisocyanates, and traditional epoxy resin crosslinkers such as polyamines and polyacids.

In the present specification, by 1,3,5-triazine carbamate is meant a compound based on one or more 1,3,5-triazine cores having on average at least two carbamate groups attached to such core or cores. Such 1,3,5-triazine carbamates and methods for preparing the same are known, for example, from commonly owned US4939213, US5084541, US5288865, EP-A-0604922 (corresponding to United States Application Serial No. 07/998,313, filed December 29, 1992), EP-A-0624577 (corresponding to United States Application Serial No. 08/061,905 filed May 14, 1993), EP-A-0649842 (corresponding to United States Application Serial No. 08/138,581, filed October 15, 1993), WO95/30663 (corresponding to United States Application Serial No. 08/239,009, filed May 6, 1994), WO96/04258 (corresponding to United States Application Serial No. 08/286,835, filed August 5, 1994), WO96/11915 (corresponding to United States Application Serial No. 08/324,549, filed October 18, 1994) and WO96/15185 (corresponding to United States Application Serial No. 08/340,950, filed November 16, 1994), all of which are hereby incorporated by reference herein for all purposes as if fully set forth.

Preferred for use in the present invention are those 1,3,5-triazine carbamates of the following general formula, as well as oligomers thereof:



wherein R is selected from the group consisting of -NHCOOR³, hydrogen, hydrocarbyl, hydrocarbyloxy, hydrocarbylthio, amido, sulfonamido, amino, hydrocarbylamino, dihydrocarbylamino and cyclic amino; and wherein each R¹, R² and R³ is independently selected from the group consisting of hydrocarbyl and hydrocarbyloxyhydrocarbyl. The term

"hydrocarbyl" in the context of the present invention, and in the above formula, is a group which contains carbon and hydrogen atoms and includes, for example, alkyl, aryl, aralkyl, alkenyl, and substituted derivatives thereof.

5 In the more preferred embodiments, R is selected from the group consisting of -NHCOOR³; hydrogen; a hydrocarbyl group having from 1 to 20 carbon atoms such as alkyl (e.g., methyl and butyl), cycloalkyl (e.g., cyclohexyl), alkenyl (e.g., vinyl), aryl (e.g. phenyl), aralkyl (e.g., benzyl) and the like; a hydrocarbyloxy group having 1 to 20 carbon atoms such as alkoxy (e.g., methoxy), aryloxy (e.g., phenoxy) and the like; hydrocarbylthio groups having 1 to 20 carbon atoms such as methylthio, phenylthio and the like; amido groups
10 such as acetamido; sulfonamido groups such as benzenesulfonamido; an amino group (e.g., -NH₂); hydrocarbylamino groups having 1 to 20 carbon atoms such as methylamino, butylamino and the like; dihydrocarbylamino groups having 2 to 40 carbon atoms such as dimethylamino; and cyclic amino groups such as pyrrolidino, piperidino, morpholino, azepino and the like. Crosslinkers wherein R is -NHCOOR³ are especially preferred.

15 As preferred R¹, R² and R³ groups may be mentioned, for example, hydrocarbyl groups having 1 to 20 carbon atoms such as alkyl (e.g., methyl and butyl), cycloalkyl (e.g., cyclohexyl), alkenyl (e.g., vinyl), aryl (e.g. phenyl), aralkyl (e.g., benzyl) and the like; and hydrocarbyloxyhydrocarbyl groups having 2 to 40 carbon atoms with the hydrocarbyl group being as described above. Further, these groups may also have a substituent such as a
20 halogen atom, a cyano group, a sulfoxide group, a sulfone group, a carbonyl group, an ester group and an amide group. Mixtures of the above are also suitable.

More preferred of the above for R¹, R² and R³ are the aliphatic alkyls and alkenyls having 1 to 8 carbon atoms, cyclic alkyls and alkenyls having 4 to 12 carbon atoms, alkoxyalkyls having 2 to 16 carbon atoms, and aryl and alkaryl having 6 to 18 carbon
25 atoms, as well as mixtures thereof. As specific preferred examples may be mentioned methyl, ethyl, propyl, n-butyl, i-butyl, t-butyl, pentyl, hexyl, cyclohexyl, heptyl, octyl, ethylhexyl, allyl, ethoxyethyl, 1-methoxy-2-propyl, phenyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, dimethylphenyls, 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl and mixtures thereof.

30 Especially preferred 1,3,5-triazine carbamate crosslinkers for use in this invention are those of the above formula wherein R is -NHCOOR³, and wherein R¹, R² and R³ are independently alkyls having 1 to 8 carbon atoms, and particularly methyl and/or butyl, which includes which includes tris-(butoxycarbonylamino)-1,3,5-triazine, tris-(methoxycarbonylamino)-1,3,5-triazine and tris-(methoxybutoxycarbonylamino)-1,3,5-
35 triazine. As a preferred example of the latter may be mention such a 1,3,5-triazine

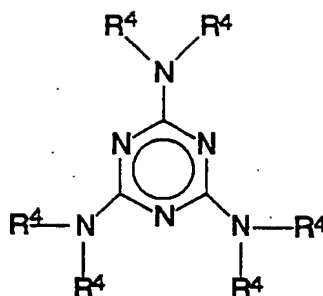
carbamate crosslinkers having a methyl to butyl molar ratio in the range of from about 0.50 to about 1.5 (as determined by Nuclear Magnetic Resonance (NMR) spectroscopy), and particularly those having methyl to butyl ratios in the range of from about 0.65 to about 1.2.

5 These 1,3,5-triazine carbamates may be prepared, for example, by the methods described in the previously incorporated US4939213, US5084541, US5288865, EP-A-0604922 (corresponding to United States Application Serial No. 07/998,313, filed December 29, 1992), EP-A-0624577 (corresponding to United States Application Serial No. 08/061,905 filed May 14, 1993), EP-A-0649842 (corresponding to United States Application Serial No. 08/138,581, filed October 15, 1993), WO95/30663 (corresponding to United States
10 Application Serial No. 08/239,009, filed May 6, 1994), WO96/04258 (corresponding to United States Application Serial No. 08/286,835, filed August 5, 1994), WO96/11915 (corresponding to United States Application Serial No. 08/324,549, filed October 18, 1994) and WO96/15185 (corresponding to United States Application Serial No. 08/340,950, filed November 16, 1994), and reference may be had thereto for further details.

15 In addition to the 1,3,5-triazine carbamate crosslinkers described in detail above, the crosslinker component may optionally comprise a variety of additional ingredients. For example, the crosslinker component may optionally contain other crosslinking agents, referred to herein as "co-crosslinkers," which include, particularly, active-hydrogen and epoxy reactive crosslinking agents such as, for example, aminoplast resins, blocked and/or
20 unblocked polyfunctional isocyanates, and traditional epoxy crosslinkers such as polyamines and polyacids.

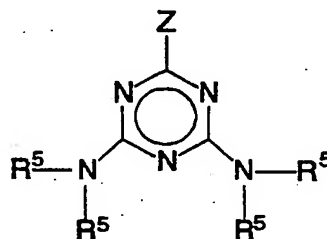
As suitable aminoplast resins may be mentioned the partially or substantially fully methylolated, partially or substantially fully etherified amino compounds based on melamine, guanamines, glycolurils and urea. In general, such aminoplast resins are well known to
25 those of ordinary skill in the art (see, for example, previously incorporated EP-A-0604922) and are generally available commercially. Most commonly, they include melamines, guanamines such as benzo-, aceto- and cyclohexylcarbo-guanamines, glycolurils and ureas, as well as the at least partially N-alkylolated and N-alkoxyalkylated derivatives thereof. The term "aminoplast resin" also includes the oligomers of such amino compounds.

30 As suitable melamine-based aminoplast resins may be mentioned those of the following general formula



10 wherein each R^4 is independently selected from H, an alkylol group and an alkoxyalkyl group. Preferred melamines are those wherein each R^4 is independently selected from H, a methylol group and an alkoxymethyl group having from 1 to 8 carbon atoms in the alkoxy group.

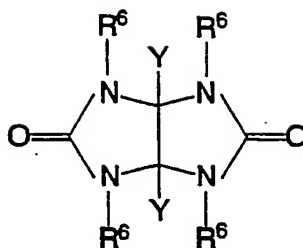
15 As suitable guanamine-based aminoplast resins may be mentioned those of the following general formula



25 wherein Z is selected from H, an alkyl group of from 1 to 20 carbon atoms, an aryl group of from 6 to 20 carbon atoms, and an aralkyl group of from 7 to 20 carbon atoms, and wherein each R^5 is independently selected from H, an alkylol group and an alkoxyalkyl group. Preferred guanamines are those wherein each R^5 is independently selected from H, a methylol group and an alkoxymethyl group having from 1 to 8 carbon atoms in the alkoxy group, and particularly wherein Z is selected from a phenyl group (benzoguanamines), a methyl group (acetoguanamines) and a cyclohexyl group (cyclohexylcarboguanamines).

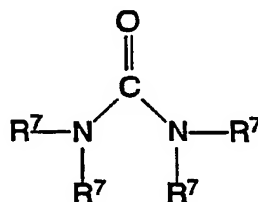
30

As suitable glycoluril-based aminoplast resins may be mentioned those of the following general formula



wherein Y is selected from H, an alkyl group of from 1 to 20 carbon atoms, an aryl group of from 6 to 20 carbon atoms, and an aralkyl group of from 7 to 20 carbon atoms, and wherein each R⁶ is independently selected from H, an alkylol group and an alkoxyalkyl group. Preferred glycolurils are those wherein each R⁶ is independently selected from H, a methylol group and an alkoxymethyl group having from 1 to 8 carbon atoms in the alkoxy group.

As suitable urea-based aminoplast resins may be mentioned those of the following general formula



wherein each R⁷ is independently selected from H, an alkylol group and an alkoxyalkyl group. Preferred ureas are those wherein each R⁷ is independently selected from H, a methylol group and an alkoxymethyl group having from 1 to 8 carbon atoms in the alkoxy group.

As specific examples of commercially available aminoplast resins of the type described above may be mentioned those sold under the trademarks CYMEL® and BEETLE® of Cytec Industries Inc. (West Paterson, New Jersey).

Polyisocyanate crosslinking agents, including blocked forms thereof, are generally well known in the art and have been extensively used in coating compositions in a monomeric, oligomeric and/or polymeric form, and preferably contain at least two reactive isocyanate groups. As specific examples of such may be mentioned hexamethylene diisocyanate; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene

diisocyanate; meta- $\alpha,\alpha,\alpha',\alpha'$ -tetramethylxylylenediisocyanate (commercially available under the trade designation m-TMXDI[®] aliphatic isocyanate from Cytec Industries Inc., West Paterson, New Jersey); para- $\alpha,\alpha,\alpha',\alpha'$ -tetramethylxylylenediisocyanate (available under the trade designation p-TMXDI[®] aliphatic isocyanate from Cytec Industries Inc., West Paterson, New Jersey); 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl cyclohexane (isophorone diisocyanate, abbreviated as IPDI); bis(4-isocyanatocyclohexyl)methane (hydrogenated MDI); biuret derivatives of various diisocyanates including, for example, hexamethylene diisocyanate (commercially available under the trade designation Desmodur[®] N of Miles Inc., Pittsburgh, Pennsylvania); uretdione derivatives of various diisocyanates including, for example, hexamethylene diisocyanate and IPDI; isocyanurate derivatives of various diisocyanates including, for example, hexamethylene diisocyanate (commercially available under the trade designation Desmodur[®] N 3390 of Miles Inc., Pittsburgh, Pennsylvania) and IPDI (commercially available under the trade designation IPDI[®] T 1890 polyisocyanate of Huls America, Inc., Piscataway, N.J.); and urethane adducts of diisocyanates with polyols such as, for example, ethylene glycol, propylene glycol, neopentyl glycol, trimethylolpropane, pentaerythritol and the like, as well as oligomeric and polymeric polyols, for example, the 3:1 meta- $\alpha,\alpha,\alpha',\alpha'$ -tetramethylxylylenediisocyanate/trimethylolpropane adduct (commercially available under the trade designation CYTHANE[®] 3160 aliphatic polyisocyanate of Cytec Industries Inc., West Paterson, New Jersey), and the 3:1 IPDI/trimethylolpropane adduct (commercially available under the trade designation SPENLITE[®] P 25-A4-60 aliphatic urethane prepolymer of Reichhold Chemicals, Research Triangle Park, North Carolina).

The polyisocyanates may be blocked in a well-known manner with, for example, lower alkyl alcohols and oximes.

Polyamine crosslinking agents for epoxy resins are also well-known to those of ordinary skill in the art and include, for example, aromatic amines such as 4,4'-diaminodiphenylmethane, 3,3'- and 4,4'-diaminodiphenylsulfone, 3,3'- and 4,4'-diaminodiphenyloxide, 3,3'- and 4,4'-diaminodiphenylsulfide, 3,3'- and 4,4'-diaminodiphenylketone, 4,4'-[1,4-phenylene-(1-methylethylidene)]-bisbenzeneamine, 1,4-phenylenediamine, 2,2-bis(4-aminophenyl)hexafluoropropane, 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, 3,4-diaminodiphenyloxide, 9,9-bis(4-aminophenyl)fluorene, 4,4'-diaminobenzanilide, 9,10-bis(4-aminophenyl)anthracene, 2,2-bis(4-[3-aminophenoxy]phenyl)sulfone, 2,2-bis(4-[4-aminophenoxy]phenyl)sulfone, 1,4-bis(4-aminophenoxy)biphenyl, bis(4-[4-aminophenoxy]phenyl)ether, 2,2-bis(4-[4-aminophenoxy]phenyl)propane and 2,2-bis([4-(4-amino-2-

trifluorophenoxy)]phenyl)hexafluoropropane; and primary and secondary aliphatic polyamines such as diethylene triamine, triethylene tetraamine, tetraethyl pentamine and ethylene diamine. Also include are amino-terminated polyarylene oligomers wherein the repeating phenyl groups are separated by either sulfide, carbonyl, sulfone carbonate or the like groups, such as amino-terminated polyarylenesulfones, polyaryleneethersulfones, polyetherketones, polyetheretherketones and like variants; and polyoxyalkylene polyamines such as polyoxypropylene diamines and triamines. These and other examples can be found in US2872427, US4607069, US4855386, US5118729 and WO94/06876, all of which are incorporated by reference herein for all purposes as if fully set forth.

Polyacid crosslinking agents for epoxy resins are likewise generally known and include, for example, monomeric polycarboxylic acids and anhydrides, and oligomeric and polymeric reaction products of such monomeric polycarboxylic acids and anhydrides with, for example, various monomeric and oligomeric polyols. Specific examples of such polyacid crosslinking agents for both liquid and powder systems can be found in US2872427, US3730930, US3752870, US3781380, US3787521, US4011381, US4346144, US4650718, US4681811, US4703101, US4764430, US5116892 and WO92/19660, all of which are incorporated by reference herein for all purposes as if fully set forth.

The Resin Component

As indicated above, the resin component comprises a polyfunctional epoxy compound. In addition, the resin component may optionally comprise a polyfunctional active hydrogen group containing compound, such as a polyfunctional hydroxy group containing resin, to impart to the crosslinked system the desired properties.

The polyfunctional epoxy compound usable as the resin component in the curable compositions of the present invention contains, on average, at least two and preferably more than two epoxy functionalities per molecule, and includes polyfunctional epoxy group containing materials which are monomeric, oligomeric, polymeric or a mixture thereof. Such polyfunctional epoxy compounds are in general well-known to those of ordinary skill in the art, as exemplified by previously incorporated US2872427, US3730930, US3752870, US3781380, US3787521, US4011381, US4346144, US4607069, US4650718, US4681811, US4703101, US4764430, US4855386, US5116892, US5118729, WO92/19660 and WO94/06876, as well as US5001173 which is also incorporated by reference herein for all purposes as if fully set forth.

As specific examples of monomeric polyfunctional epoxy compounds may be mentioned difunctional epoxy resins (bisepoxides) including glycidyl ethers of dihydric

phenols like the bisphenol-A/epichlorohydrin reaction products such as diglycidyl bisphenol-A; vinyl cyclohexene diepoxides such as 4-vinyl-1-cyclohexene diepoxide; 1,2,5,6-diepoxyoctane; 1,2,7,8-diepoxyoctane; dicyclopentadiene diepoxide; 1,4-divinyl benzene diepoxide; cyclohexene-4-methyl cyclohexene-4-carboxylate diepoxide; glycidylated diol type polyfunctional epoxy group containing materials such as hexane diol diglycidyl ether, ethylene glycol diglycidyl ether, diethylene glycol diglycidyl ether, triethylene glycol diglycidyl ether and the like. Other suitable monomeric polyfunctional epoxy compounds include trifunctional epoxy resins (trisepoxides) such as tri-(4-glycidyl oxyphenyl)methane and triglycidyl isocyanurate; and higher polyfunctional epoxides such as glycidylated pentaerythritol and sorbitol. As a commercially available example of bisphenol-A/epichlorohydrin reaction products may be mentioned epoxy resins sold under the trade designation Epon[®] of Shell Chemical Company (Houston, TX), such as Epon[®] 828 resin having an equivalent weight in the range of 185 to 192. As a commercially available example of a glycidylated sorbitol may be mentioned the substantially monomeric glycidylated sorbitol known as Synocure[®] 888 H resin (Cook Composites and Polymers Company, Port Washington, Wisconsin).

The oligomeric polyfunctional epoxy group containing materials include oligomeric forms of the monomeric materials, oligomers of diepoxides such as low molecular weight bis-phenol-A oligomers, prepolymers thereof, reaction products of amines with diepoxides, and the like.

The polymeric polyfunctional epoxy group containing materials include, for example, polymers of epoxy group containing unsaturated monomers and copolymers thereof with unsaturated comonomers which do not contain epoxy groups. As examples of the epoxy group containing unsaturated monomers may be mentioned glycidyl acrylate, glycidyl methacrylate and allyl glycidyl ether. As examples of the unsaturated comonomers which do not contain epoxy groups may be mentioned the alkyl esters of acrylic and methacrylic acid containing from 1 to 20 carbon atoms in the alkyl group, such as methyl acrylate, ethyl acrylate, butyl acrylate, ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and ethylhexyl methacrylate; vinyl aromatic compounds such as styrene, methyl styrene and vinyl toluene; vinyl and vinylidene halides such as vinyl and vinylidene chlorides, vinyl esters such as vinyl acetate; allyl alcohol; and hydroxyalkyl acrylates and methacrylates containing from 1 to 20 carbon atoms in the hydroxyalkyl group, such as hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate and the like. The copolymerization reaction may be carried out by known methods such as that described in various of the aforementioned incorporated reference

as well as in US3787521, US4181642, EP-A-0480120 and EP-A-0256369, which are also incorporated by reference herein as if fully set forth.

Commercially available examples of glycidyl methacrylate copolymer type polyfunctional epoxy group containing materials include Synthacryl[®] VCS 1436 resin a product of Hoechst-Celanese Corporation, Charlotte, NC; Estron[®] GMA-252 resin (Mw: 8300; EW: 250; Tg: 36), a product of Estron Chemicals, Calvert City, KY; Almatex[®] PD 6100 (Mw: 12500; EW: 1030; Tg: 63), Almatex[®] PD 6300, Almatex[®] PD 7110, Almatex[®] PD 7210, Almatex[®] PD 7310, Almatex[®] PD 7610 (Mw: 7000; EW: 510; Tg: 45) and Almatex[®] PD 1700 resins, products of Mitsui Toatsu Company, Inc. of Japan, and available from Anderson Development Company, Adrian, MI; and Blemmer[®] CP-15 (Mw: 12300; EW: 1000; Tg: 63), Blemmer[®] CP-30 P (Mw: 10300; EW: 530; Tg: 62) and Blemmer[®] CP-5 SA (Mw: 10100; EW: 3000; Tg: 96) resins, products of Nippon Oil and Fat Corporation of Japan.

As indicated above, the resin component may optionally include a polyfunctional active hydrogen group containing compound. Active hydrogen-containing functionality, as utilized herein, refers to functional groups which contain active hydrogens reactive with the epoxy groups of the polyfunctional epoxy compound and/or with the carbamate groups of the triazine carbamate (or functionality which may be generated by the carbamate groups under cure conditions, such as isocyanate functionality). Such active hydrogen functionality is in general well-known to those of ordinary skill in the art and includes, most commonly, hydroxyl, carboxyl and amino groups. When utilized herein, hydroxyl is preferred.

Suitable such polyfunctional hydroxy group containing materials are again generally well known to those skilled in the art, and contain at least two and preferably more than two hydroxy groups. Reference may be had to previously incorporated US4939213, US5084541, US5288865, EP-A-0604922 (corresponding to United States Application Serial No. 07/998,313, filed December 29, 1992), EP-A-0624577 (corresponding to United States Application Serial No. 08/061,905 filed May 14, 1993), EP-A-0649842 (corresponding to United States Application Serial No. 08/138,581, filed October 15, 1993), WO95/30663 (corresponding to United States Application Serial No. 08/239,009, filed May 6, 1994), WO96/04258 (corresponding to United States Application Serial No. 08/286,835, filed August 5, 1994), WO96/11915 (corresponding to United States Application Serial No. 08/324,549, filed October 18, 1994) and WO96/15185 (corresponding to United States Application Serial No. 08/340,950, filed November 16, 1994), for further details.

As examples of preferred polyfunctional hydroxy group containing materials may be mentioned acrylic or polyester backbone resins. Illustrative examples include acrylic resins

which may be obtained by the copolymerization of acrylic or methacrylic esters with hydroxyfunctional acrylic or methacrylic esters such as hydroxyethyl acrylate or methacrylate, optionally with simultaneous use of additional vinyl compounds such as, for example, styrene. Illustrative examples of the polyfunctional hydroxy group containing materials also include polyester resins which may be obtained, for example, by the reaction of polycarboxylic acids with excess quantities of polyhydric alcohols. Other suitable polyfunctional hydroxy group containing resins include polyurethane prepolymers, alkyds, as well as hydroxy group containing epoxy prepolymers such as those resulting from the reaction of a polyfunctional epoxy group containing compound with an amine or with a polyfunctional carboxylic acid derivative.

In general, such resins may have pendent or terminal hydroxyl functionalities and preferably have the following characteristics: weight average molecular weights (Mw) of from about 750 to about 7000, and more preferably from about 2000 to about 5000; and hydroxyl numbers of from about 20 to about 100 mg KOH/g resin, more preferably from about 25 to about 60 mg KOH/g resin, and especially from about 25 to about 40 mg KOH/g resin.

For waterborne applications, polyfunctional hydroxy group containing materials having thereon aqueous dispersion promoting groups such as carboxylic or sulfonic functionalities and higher molecular weights are generally usable, such as disclosed in previously incorporated United States Application Serial No. 08/340,950 (filed November 16, 1994), as well as GB1530022, EP-A-0568134, EP-A-0663413, US5075370 and US5342878, all of which are further incorporated by reference herein as if fully set forth. Solid polyfunctional hydroxy group containing materials are suitable for use in powder coatings. For solvent borne coatings, liquid polyfunctional hydroxy group containing materials are preferred. However, solid polyfunctional hydroxy group containing materials may be used in cases when the solids are soluble in the solvent used in a particular formulation. Specific suitable hydroxyl functional resins will be readily recognized by those of ordinary skill in the art depending upon the desired end use.

Commercially available examples of polyfunctional hydroxy group containing materials include JONCRYL[®] 500 acrylic resin, a product of S.C. Johnson & Sons, Racine, WI; ACRYLOID[®] AT-400 acrylic resin, a product of Rohm & Haas, Philadelphia, PA; CYPLEX[®] 1531 polyester resin, a product of Cytec Industries, West Paterson, NJ; CARGILL 3000 and 5776 polyester resins, products of Cargill, Minneapolis, MN; TONE[®] polyester resin, a product of Union Carbide, Danbury, CT; K-FLEX[®] XM-2302 and XM-2306 resins, products of King Industries, Norwalk, CT; CHEMPOL[®] 11-1369 resin, a product of Cook

Composites and Polymers, Port Washington, WI; JONCRYL[®] 540 acrylic emulsion polymer, a product of S.C. Johnson & Sons, Racine, WI; RHOPLEX[®] AC-1024 acrylic emulsion resin, a product of Rohm & Haas, Philadelphia, PA; XC[®] 4005 water reducible acrylic resin, a product of Cytec Industries, West Paterson, NJ; CRYLCOAT[®] 3494 solid hydroxy terminated polyester resin, a product of UCB CHEMICALS USA, Smyrna, GA; RUCOTE[®] 101 polyester resin, a product of Ruco Polymer, Hicksville, NY; JONCRYL[®] SCX-800-A and SCX-800-B hydroxyfunctional solid acrylic resins, products of S.C. Johnson & Sons, Racine, WI); and ALFTALAT[®] AN 745 hydroxyfunctional polyester resin, a product of Hoechst Corporation.

10 Other Ingredients

In addition to the crosslinker and resin components described in detail above, the curable compositions of the present invention may optionally comprise a variety of additional ingredients normal for any particularly chosen end use.

One common such additional ingredient is a cure catalysts for increasing the cure rate and thereby reducing the cure temperature and/or cure time of the systems described herein. As examples of cure catalysts may be mentioned basic catalysts, organometallic catalysts and acidic catalysts.

As examples of basic catalysts may be mentioned quaternary onium compounds such as ammonium, phosphonium and sulfonium compounds, as well as salts thereof having a counterion such as hydroxide, alkoxide, aryloxide, carboxylate, carbonate and the like. As examples of quaternary onium salts may be mentioned quaternary ammonium salts, quaternary phosphonium salts and quaternary sulfonium salts. Of these, quaternary ammonium salts such as quaternary ammonium hydroxides, quaternary ammonium alkoxides, quaternary ammonium carboxylates and quaternary ammonium carbonates are preferred. Quaternary ammonium hydroxides such as benzyl trialkylammonium hydroxides are especially preferred.

As examples of other basic catalysts may be mentioned strong nitrogenous bases such as amines, imines, amidines and guanidines, and inorganic bases such as alkali metal salts. Suitable alkali metal salts include salts of lithium, sodium or potassium having a counterion such as hydroxide, alkoxide, aryloxide, carboxylate, carbonate and the like. Suitable amines include primary, secondary, and tertiary amines. Tertiary amines are preferred to primary and secondary amines and include trialkyl amines, triaryl amines, alkyl diaryl amines, dialkyl aryl amines, cyclic amines, bicyclic amines, polycyclic amines, heteroaromatic amines and mixtures thereof, including heteroaromatic amines such as 4-pyrrolidinopyridine, 4-piperidopyridine, and 4-morpholinopyridine, and bicyclic amines

such as 1,4-diaza-(2.2.2)-bicyclooctane (DABCO). Of these other basic catalysts, 1,4-diaza-(2.2.2)-bicyclooctane (DABCO) and alkylated guanidines such as tetramethylguanidine are preferred.

5 As examples of organometallic catalysts may be mentioned organotin compounds such as dibutyltin di-2-ethylhexoate, dibutyltin diisooctyl maleate, dibenzyltin di-2-ethylhexoate, dibutyltin dilaurate, dimethyltin dilaurate, tetrabutyl diacetoxystannoxane, tetramethyl diacetoxystannoxane, tetrapropyl diacetoxystannoxane, dibutyltin dichloride and the like.

10 As examples of acidic catalysts may be mentioned sulfonic acids (such as p-toluene sulfonic acid or dodecyl benzene sulfonic acid), aryl and alkyl acid-phosphates and pyrophosphates, carboxylic acids, sulfonimides and mineral acids. Latent acidic catalysts, such as amine-blocked p-toluene sulfonic acid or amine-blocked dodecyl benzene sulfonic acid, are included within the meaning of acidic catalysts.

15 If an amino resin co-crosslinker is utilized with the 1,3,5-triazine carbamate crosslinker, an acid catalyst will be most suitable. If a polyisocyanate co-crosslinker is utilized with the 1,3,5-triazine carbamate crosslinker, a basic and/or an organometallic catalyst will be most suitable. If a 1,3,5-triazine carbamate crosslinker and a polyfunctional epoxy group containing material only are used, a quaternary catalyst such as benzyltrimethylammonium acetate, tetrabutylammonium acetate and tetrabutylammonium bromide would be most suitable. Again, however, cure catalysts are optional in the present systems and, when utilized, are generally added in amounts ranging from about 0.001 wt % to about 6.0 wt %, and preferably up to about 2.0 wt %, based on the combined weight of the backbone resin and crosslinker components (total resin solids).

25 The present curable compositions may also contain a solvent of the type typically found in coatings applications including, for example, alcohols, ketones, esters, aliphatic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons and the like. In waterborne coating applications, the curable compositions may contain, in addition to water, a co-solvent and an aqueous dispersion promoting material such as ethylhexanol, Texanol® (a C8-hydroxyalkyl ester of methylpropionic acid commercially available from Eastman Chemical Company), surfactants and other related materials.

30 Other optional ingredients may be additionally used depending on the particular application. For example, well known auxiliaries and additives typically utilized in the coatings industry include foam inhibitors, levelling aids, pigments, dispersants such as pigment dispersing aids, dyes, UV absorbers (including hydroxy aryl triazine types (such as CYAGARD® UV 1164 of Cytec Industries Inc.), benzotriazole types and benzophenone

types), heat stabilizers, other stabilizing additives such as antioxidants, hindered amine light stabilizers (such as Sanduvor® 3058 of Clariant) and the like. Other such optional ingredients have been exemplified in the many previously incorporated references, and reference may be had thereto for further details. Reference may specifically be had to
5 US4426471, US4344876, US4619956, US5106891, US5322868, US5461151, EP-A-0434608, EP-A-0444323 and EP-A-0704437, all of which are incorporated by reference herein as if fully set forth, for detailed discussions of the stabilization of coatings and other curable compositions with UV absorbers, hindered amine light stabilizers and/or other types of light stabilizers.

Preparation and Uses of the Curable Compositions

The curable compositions of the present invention are suitable for numerous uses including, for example, as coatings and adhesives, in decorative laminated boards, and in the formation of crosslinked molded articles such as engineering composites. The curable
15 compositions may be prepared by admixing the various components via methods and in relative amounts which are recognizable by those of ordinary skill in the art in the relevant field depending upon the particular end use chosen. As a general rule, the resin component and the crosslinker component should preferably be admixed in an equivalents ratio (equivalents of reactive functionality) of from about 0.5:1 to about 2:1, and more preferably from about 0.8:1 to about 1.2:1.

An especially preferred use of the curable compositions in accordance with the present invention is in the coatings field. Any conventional type of coating may be prepared using the curable compositions described herein, including organic solvent based liquid coatings, waterborne coatings and powder coatings. In coatings applications, the weight
25 amounts of 1,3,5-triazine carbamate crosslinker and polyfunctional epoxy compound will be dependent upon factors including, for example, the particular materials chosen, the presence of other reactive species as well as the desired end use. Based upon these variables and others, those of ordinary skill in the art should be able to adjust the composition of the coatings (including the relative amounts of the components) to achieve
30 the desired effect. It is, however, preferred that when the 1,3,5-triazine carbamate crosslinker and polyfunctional epoxy compound comprise the major reactive portion of the coating composition, they be present in a 1,3,5-triazine carbamate crosslinker to polyfunctional epoxy compounds equivalents ratio in the range of from about 0.5:1 to about 2:1, and especially in the range of from about 0.8:1 to about 1.2:1. When polyfunctional
35 hydroxy group containing and/or co-crosslinkers are additionally employed, it is preferred

that the overall crosslinker component to resin component equivalents ratio be within the above indicated ranges.

Organic solvent based liquid coatings in accordance with the present invention may be prepared via conventional means by adding into a commonly used organic coatings solvent the components of the curable composition and the optional ingredients, if present, in any convenient order. In organic solvent based coatings, the systems are formulated to produce a solids content level suitable for convenient application with minimal material loss, preferably at a solids content level in the range of from about 20 weight percent to about 85 weight percent, and more preferably at a solids content level in the range of from about 45 weight percent to about 80 weight percent, depending on the method of application chosen.

Waterborne coating compositions in accordance with the present invention may be prepared by combining the components of the coating in any particular order, but it is preferred to do so by preparing a dispersible composition by substantially homogeneously mixing the coating components with a surface active material (which may be an inherent property of the resin component), then dispersing the dispersible composition in an aqueous medium, which may comprise solely water or may contain other components such as minor amounts of water-miscible co-solvents to ease dispersion or adjust viscosity. The waterborne coating compositions may be formulated to various solids contents, generally ranging from about 20% to about 75% by weight solids, but preferably in the range of from about 30% to about 55% by weight solids, depending on the method of application chosen.

Powder coating compositions in accordance with the present invention may be prepared by any well-known method, for example, by dry mixing the components in a mixer or blender followed by compounding in an extruder and granulating, grinding and then screening to obtain a powder of suitable mesh size for powder coating. For powder coatings applications, compositions containing solid crosslinker and backbone resin components are preferred. Alternatively, some or all of the components may be dissolved in a solvent such as methylene chloride and spray dried by well known techniques. Moreover, it may be preferable to masterbatch the crosslinking agent and the hydroxyl functional resin prior to mixing the optional components of the composition in a manner well known to a person skilled in the art.

The present coating compositions are utilized by applying the coating to a substrate then curing the so-applied coating to form crosslinked films. Liquid coatings may be applied, for example, by dipping, spraying, padding, brushing, flowcoating, electrocoating or electrostatic spraying. After application, the liquid carrier (e.g., organic solvent and/or

water) is generally allowed to partially evaporate to produce a uniform coating on the substrate. Powder coatings may be applied, for example, by means such as a powder gun, electrostatic deposition or deposition from a fluidized bed. After deposition, the powder is typically heated usually to a temperature sufficient to cause the particles to soften, melt, flow and begin to cure.

Full curing of the present coating compositions (and curable compositions) requires elevated temperatures generally in the range of from about 25°C to about 450°C depending on the components as well as the end use application. In liquid coatings applications, the cure temperature is typically in the range of from about 80°C to about 160°C. In powder coatings applications, the cure temperature is typically in the range of from about 110°C to about 230°C, preferably from about 150°C to about 220°C, and most preferably from about 170°C to about 200°C. In coil coatings applications, the cure temperature is typically in the range of from about 250°C to about 450°C. Cure time preferably is in the range of from about 1 second to about 30 minutes but may vary depending on the temperature chosen for cure. For example, a fully cured coil coating may be obtained by either curing at 260°C for 1 minute or by curing at 417°C for 20 seconds. Typical cure times for liquid and powder coatings are in the range of from about 5 minutes to about 30 minutes.

The coating compositions of this invention may be formulated for use in numerous areas such as original equipment manufacturing (OEM) including automotive coatings, general industrial coatings including industrial maintenance coatings, architectural coatings, can coatings and the like. They are usable as coatings for wire, appliances, automotive parts, furniture, pipes, machinery, and the like. The present systems can replace 1K urethane coatings in applications such as acid etch resistant automotive finishes, powder coatings, coil coatings including base coats and top coats. Suitable surfaces include metals such as steel and aluminum, plastics, wood, and glass.

The examples which follow are intended to be illustrative of certain preferred embodiments of the invention and are not to be construed to limit the invention in any manner. In the following examples, all amounts are expressed as parts by weight, unless otherwise stated.

EXAMPLE 1

Various coating formulations were prepared by admixing the components listed in the tables below with sufficient solvent to produce a liquid coating composition having about 50 weight percent solids. The coatings were applied onto Bonderite® 1000 CRS panels (ACT Laboratories, Inc., Hillsdale, Michigan) and, after about 5 minutes at room temperature

to flash off some of the volatiles, the coated panels were heated to the indicated bake temperature for curing. Upon cure, the panels were cooled to room temperature and the film and resistance properties were determined. The results are summarized in Tables 1 to 6.

5

Table 1: Cure Response of Synthacryl® VCS 1436/Triazine Carbamate Coatings

<u>Coatings</u>		<u>A</u>	<u>B</u>	<u>C</u>
10	• Synthacryl® VCS 1436 Resin(60 wt% in MIBK)	13.46	13.46	13.46
	• Tris-(methoxybutoxycarbonylamino)-1,3,5-triazine (50 wt% in n-Butanol; Methyl to n-Butyl mole ratio: 41/59)	3.85	----	3.85
	• Benzyltrimethylammonium Acetate (25 wt% in Xylene/MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1)	0.60	0.60	----
15	• Dow Corning Paint Additive 57 (10 wt% in Arcosolv® PM Acetate)	0.05	0.05	0.05
20	• Solvent: Xylene/MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1	2.00	2.50	2.60
	<u>Coating Performance (125°C /30 minutes bake)</u>			
	Film thickness, mils	1.5	1.4	1.3
25	Film hardness, KHN ₂₅	17.8	17.8	16.2
	Pencil hardness	2H-3H	F-H	2B-B
	MEK rubs	25/200+	5/75	1/5
30	<u>Coating Performance (140°C/30 min bake)</u>			
	Film thickness, mils	1.4	1.3	1.0
	Film hardness, KHN ₂₅	18.6	17.6	16.2
	Pencil hardness	2H-3H	F-H	2B-B
	MEK rubs	200/200+	5/100	1/5

Table 2: Acid Etch Resistance of Synthacryl® VCS 1436/Triazine Carbamate Coatings

<u>Coating</u>		<u>D</u>
5	• Synthacryl® VCS 1436 Resin (60 wt% in MIBK)	26.92
	• Tris-(methoxybutoxycarbonylamino)-1,3,5-triazine (50 wt% in n-Butanol; Methyl to n-Butyl mole ratio: 41/59)	19.25
	• Benzyltrimethylammonium Acetate (25 wt% in Xylene/MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1)	1.2
10	• Cyagard® UV 1164 light stabilizer (20 wt% in Xylene/MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1)	2.00
	• Sanduvor® 3058 Liquid (10 wt% in Xylene/MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1)	1.00
15	• Dow Corning Paint Additive 57 (10 wt% in Arcosolv® PM Acetate)	0.10
	• Solvents: Xylene/MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1	1.08
20	<u>Coating Performance (140°C /30 minutes bake)</u>	
	Film thickness, mils	1.7
	Film hardness, KHN ₂₅	17.4
	Pencil hardness	2H-3H
	MEK rubs	200+/200+
25	<u>Acid Etch Resistance Test⁽¹⁾</u>	
	<u>Acid Used</u>	<u>Extent of Attack</u>
	0.1N H ₂ SO ₄ (aq)	1
	0.1N H ₃ PO ₄ (aq)	0
30	0.1N NaOH (aq)	0
	100 ppm H ₂ SO ₄ (aq)	0
	Ford # 24 Acid ⁽¹⁾	2

(1) The Ford #24 Acid used for the environmental etch resistance test was prepared by admixing the following ingredients in the indicated amounts: (a) 90 weight % aqueous formic acid: 47 grams; (b) 10 weight % aqueous solution of tannic powder: 24 grams; (c) honey: 24 grams; and (d) 10 weight % aqueous solution of albumin: 5 grams. The acid solution prepared in this manner (4 drops) and the coating were contacted and baked at 60°C for 30 minutes. Thereafter, on a scale of 0 to 10, with 0 corresponding to no attack and 10 corresponding to severe attack, a numerical value was assigned indicating the extent of attack on the coating by the acid. Effect of the other acids were determined in the same manner.

10

Table 3: Catalysts for Almatex® PD 7610/Triazine Carbamate Coatings

<u>Coating</u>		E	F	G	H
5	• Almatex® PD 7610 Resin (60 wt % in MIBK)	13.46	13.46	13.46	13.46
	• Tris-(methoxybutoxycarbonylamino)-1,3,5-triazine (50 wt% in n-Butanol; Methyl to n-Butyl mole ratio: 41/59)	3.85	3.85	3.85	3.85
	• Benzyltrimethylammonium Acetate (25 wt% in Xylene/MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1)	0.60	---	---	---
10	• 1,4-Diazabicyclo[2.2.2]octane (20 wt% in Xylene/MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1)	---	0.75	---	---
	• Tetrabutylammonium Acetate (20 wt% in Xylene/MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1)	---	---	0.75	---
15	• Tetrabutylammonium Bromide (20 wt% in Xylene/MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1)	---	---	---	0.75
	• Dow Corning Paint Additive 57 (20 wt% in Arcosolv® PM Acetate)	0.10	0.10	0.10	0.10
20	• Solvents: Xylene/MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1	1.99	1.84	1.84	1.84
25	<u>Coating Performance</u>				
	Bake Schedule, °C/min	125/30	125/30	120/30	120/30
	Film thickness, mils	1.6	1.5	1.5	1.5
	Film hardness, KHN ₂₅	17.2	16.2	17.6	17.6
30	Pencil hardness	2H-3H	H-2H	2H-3H	2H-3H
	MEK rubs	100/200+	50/200+	75/200+	75/200+

Table 4: Epon® 828 Coatings With and Without Triazine Carbamate

<u>Coating</u>		<u>I</u>	<u>J</u>
5	• Epon® 828 resin	6.1	6.1
	• Tris-(methoxybutoxycarbonylamino)-1,3,5-triazine (50 wt % in n-Butanol; Methyl to n-Butyl mole ratio: 41/59)	7.8	----
	• Benzyltrimethylammonium Acetate (25 wt% in Xylene/ MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1)	0.3	0.3
10	• Dow Coming Paint Additive 57 (10 wt% in Arcosolv® PM Acetate)	0.1	0.1
	• Solvents: Xylene/MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1	5.7	13.5
15	<u>Coating Performance (110°C/30 minutes Bake)</u>		
	Film thickness, mils	1.0	1.0
	Film hardness, KHN ₂₅	20	<1
	Pencil hardness	H-2H	3B-2B
	MEK rubs	50/200+	1/20
20	<u>Coating Performance (125°C/30 minutes Bake)</u>		
	Film thickness, mils	1.0	1.0
	Film hardness, KHN ₂₅	20	2.5
	Pencil hardness	3H-4H	2B-B
	MEK rubs	200+/200+	10/50
25			

Table 5: Effect of Catalyst Levels on Epon® 828/Triazine Carbamate Coatings

Coatings		K	L	M
5	• Epon® 828 resin	6.1	6.1	6.1
	• Tris-(methoxybutoxycarbonylamino)-1,3,5-triazine (50 wt% in n-Butanol; Methyl to n-Butyl mole ratio: 41/59)	7.8	7.8	7.8
	• Benzyltrimethylammonium Acetate (25 wt% in Xylene/MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1)	1.2	0.6	0.3
10	• Dow Corning Paint Additive 57 (10 wt% Arcosolv® PM Acetate)	0.1	0.1	0.1
	• Solvents: Xylene/MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1	3.6	4.2	4.5
15	<u>Coating Performance (100°C/30 minutes Bake)</u>			
	Film thickness, mils	1.0	1.0	1.0
	Film hardness, KHN ₂₅	19.8	19.6	5.5
	Pencil hardness	2H-3H	2B-B	3B-2B
20	MEK rubs	50/200+	1/10	1/10
	<u>Coating Performance (110°C/30 minutes Bake)</u>			
	Film thickness, mils	1.0	1.0	1.0
	Film hardness, KHN ₂₅	20.9	20.6	20.4
25	Pencil hardness	3H-4H	3H-4H	3H-4H
	MEK rubs	200+/200+	200+/200+	50/200+
	<u>Coating Performance (125°C/30 minutes Bake)</u>			
	Film thickness, mils	1.0	0.9	0.95
30	Film hardness, KHN ₂₅	22.0	23.0	22.0
	Pencil hardness	3H-4H	3H-4H	3H-4H
	MEK rubs	200+/200+	200+/200+	200+/200+

Table 6: Synocure® 888 H/Triazine Carbamate Coatings

	<u>Coatings</u>	<u>N</u>	<u>O</u>
	• Synocure® 888 H resin	65	100
5	• Tris-(methoxybutoxycarbonylamino)-1,3,5-triazine (50 wt% in n-Butanol; Methyl to n-Butyl mole ratio: 41/59)	70	----
	• Benzyltrimethylammonium Acetate (25 wt% in Xylene/MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1)	6.0	6.0
10	• Dow Corning Paint Additive 57 (10 wt% Arcosolv® PM Acetate)	1.0	1.0
	• Solvents: Xylene/MIBK/Arcosolv® PM Acetate, weight ratio of 1:1:1	43.2	78.2
15	<u>Coating Performance (100°C/30 minutes Bake)</u>		
	Film thickness, mils	1.48	no cure
	Film hardness, KHN ₂₅	11.5	no cure
	MEK rubs	125/200+	no cure
20	<u>Coating Performance (125°C/30 minutes Bake)</u>		
	Film thickness, mils	1.57	no cure
	Film hardness, KHN ₂₅	15.4	no cure
	MEK rubs	200+/200+	no cure
25	<u>Coating Performance (140°C/30 minutes Bake)</u>		
	Film thickness, mils	1.55	no cure
	Film hardness, KHN ₂₅	18.4	no cure
	MEK rubs	200+/200+	no cure
30			

EXAMPLE 2

Coatings with EPON® 828 resin and tris-(butoxycarbonylamino)-1,3,5-triazine cured with tetrabutyl diacetoxystannoxane (TK-1)

5 EPON® 828 resin (5.7 g) was added to the triazine carbamate (4.26 g) dissolved in 1-methoxy-2-propanol (6.0 g). The mixture was warmed on a hot water bath and to the clear solution TK-1 catalyst (0.200 g) was added. After vigorous agitation for a few minutes, the mixture was applied to Bonderite® 1000 steel panels using a #40 wire cator applicator. The panels so prepared were heated at 150°C for 30 minutes to obtain fully cured coatings
10 having 200+/200+ MEK double rubs (no marring).

COMPARATIVE EXAMPLE 1

Attempted preparation of coatings with EPON® 828 resin with catalyst

15 EPON® 828 resin (10.0 g) was dissolved in 1-methoxy-2-propanol (6.0 g). The mixture was warmed on a hot water bath and to the solution TK-1 catalyst (0.200 g) was added. After vigorous agitation for a few minutes, the solution was applied to Bonderite® 1000 steel panels using a #40 wire cator applicator, and the panels so prepared were heated at 180°C for 30 minutes. Cured coatings were not formed, indicating that EPON®
20 828 did not produce cured coatings in the presence of a catalyst under the conditions of Example 2 without the presence of the triazine carbamate crosslinker.

EXAMPLE 3

25 Coatings with EPON® 828 resin and tris-(butoxycarbonylamino)-1,3,5-triazine cured with dimethyltin dilaurate (UL-28)

 EPON® 828 resin (5.7 g) was added to the triazine carbamate (4.26 g) dissolved in 1-methoxy-2-propanol (6.0 g). The mixture was warmed on a hot water bath and to the clear solution UL-28 catalyst (0.200 g) was added. After vigorous agitation for a few
30 minutes, the mixture was applied to Bonderite® 1000 steel panels using a #40 wire cator applicator. The panels so prepared were heated at 180°C for 30 minutes to obtain fully cured coatings having 200+/200+ MEK double rubs (no marring).

EXAMPLE 4Coatings with EPON® 828 resin and tris-(butoxycarbonylamino)-1,3,5-triazine cured without catalyst

5 EPON® 828 resin (5.7 g) was added to the triazine carbamate (4.26 g) dissolved in 1-methoxy-2-propanol (6.0 g). The mixture was warmed on a hot water bath with vigorous agitation for a few minutes and applied to Bonderite® 1000 steel panels using a #40 wire cator applicator. The panels so prepared were heated at 180°C for 30 minutes to obtain fully cured coatings having 200+/200+ MEK double rubs (no marring).

COMPARATIVE EXAMPLE 2Attempted preparation of coatings with EPON® 828 resin without catalyst

15 EPON® 828 resin (10.0 g) was dissolved in 1-methoxy-2-propanol (6.0 g). The mixture was warmed on a hot water bath with vigorous agitation for a few minutes. The solution was applied to Bonderite® 1000 steel panels using a #40 wire cator applicator, and the panels so prepared were heated at 180°C for 30 minutes. Upon the first MEK rub, the coating was removed indicating that EPON® 828 by itself did not produce cured coatings under the conditions of Example 4 without the presence of the triazine carbamate crosslinker.

EXAMPLE 5

25 A white pigmented powder coating composition containing ingredients listed in Table 7 was formulated. The ingredients were premixed in a Waring blender, melt-mixed on a Brabender two-roll mill, crushed in a Waring blender, milled in a Mikro-ACM mill classifier and sprayed electrostatically onto Bonderite® 1000 steel panels with a Wagner gun. The resulting powder coating was cured by heating at the specified temperature and time. The results are summarized in Table 7.

Table 7: Preparation of Powder Coatings with Tris-(butoxycarbonylamino)-1,3,5-triazine

<u>Coating</u>		<u>P</u>
5	• Epon® 1007 F resin	85
	• tris-(butoxycarbonylamino)-1,3,5-triazine	15
	• Tetrabutyl diacetoxystannoxane (TK-1)	0.20
	• Benzoin	1.4
	• R 960 pigment (TiO ₂)	40.0
	• Resiflow P-67 flow control agent	1.3
10		
	<u>Coating Performance</u>	<u>150°C/20 min. bake</u> <u>190°C/20 min. Bake</u>
	Film thickness, mils	4.0-5.2 2.4-8.0
	Film hardness, KHN ₂₅	12.4 12.7
	Pencil hardness	H-2H H-2H
15	MEK rubs	200+/200+ 200+/200+
	Film appearance	Tight orange peel Tight orange peel
		Surface not well Surface not well
		wetted wetted
	Impact F/R (in.lbs)	40/5- 20/5-
20	Yellow index	-1.08 0.18
	Gloss 60 degrees	53.4 13.3
	20 degrees	12.7 3.5
	Gel time (seconds)	50 50
	Gel temperature (°C)	200 200
25	Vertical plate flow:	
	Distance (cm)	2.0 2.0
	Temperature (°C)	190 190
	Time (min.)	20 20

30 Although the present invention is described with reference to certain preferred embodiments, it is apparent that variations and modifications thereto may be made by those of ordinary skill in the art without departing from the scope of this invention as defined by the appended claims.

CLAIMS

1. A curable composition, comprising:

- 5 (1) a resin component comprising a polyfunctional epoxy compound; and
 (2) a crosslinker component comprising one or more compounds containing functionality reactive with the epoxy groups of the polyfunctional epoxy compound,

characterized in that the crosslinker component comprises a 1,3,5-triazine carbamate.

10 2. The curable composition of claim 1, characterized in that the 1,3,5-triazine carbamate crosslinker is a compound of the following general formula, as well as oligomers thereof:



20 wherein R is selected from the group consisting of -NHCOOR³, hydrogen, hydrocarbyl, hydrocarbyloxy, hydrocarbylthio, amido, sulfonamido, amino, hydrocarbylamino, dihydrocarbylamino and cyclic amino; and wherein each R¹, R² and R³ is independently selected from the group consisting of hydrocarbyl and hydrocarbyloxyhydrocarbyl.

25 3. The curable composition of claim 2, characterized in that R is -NHCOOR³, and R¹, R² and R³ are each independently an alkyl group of 1 to 8 carbon atoms.

30 4. The curable composition of claim 1, characterized in that the crosslinker component further comprises a co-crosslinker selected from the group consisting of aminoplast resins, blocked polyfunctional isocyanates, unblocked polyfunctional isocyanates, polyamines and polyacids.

35 5. The curable composition of claim 1, characterized in that the polyfunctional epoxy compound contains, on average, at least two epoxy functionalities per molecule.

6. The curable composition of claim 5, characterized in that the polyfunctional epoxy compound is a bisepoxide selected from glycidyl ethers of dihydric phenols.
7. The curable composition of claim 5, characterized in that the polyfunctional epoxy compound is a copolymer of an epoxy group containing unsaturated monomer with an unsaturated comonomer which does not contain epoxy groups.
8. The curable composition of claim 1, characterized in that the resin component further comprises a polyfunctional active hydrogen group containing compound.
9. The curable composition of claim 1, characterized in that the curable composition further comprises a cure catalyst.
10. The curable composition of claim 9, characterized in that the cure catalyst is selected from the group consisting of a basic catalyst, an organometallic catalyst and an acidic catalyst.
11. The curable composition of claim 10, characterized in that the cure catalyst is a basic catalyst selected from the group consisting of quaternary onium compounds and salts thereof.
12. The curable composition of claim 10, characterized in that the cure catalyst is an organometallic catalyst selected from organotin compounds.
13. The curable composition of claim 1, characterized in that the resin component and the crosslinker component are present in an equivalents ratio in the range of from about 0.5:1 to about 2:1.
14. The curable composition of claim 1, characterized in that the curable composition further comprises a light stabilizer selected from the group consisting of a UV absorber, a hindered amine light stabilizer and mixtures thereof.
15. The curable composition of claim 1, characterized in that curable composition further comprises a light stabilizer selected from the group consisting of a hydroxy aryl triazine UV absorber, a hindered amine light stabilizer and mixtures thereof.

16. The curable composition of claim 1, characterized in that the composition is in the form of an organic solvent based liquid system.

5 17. The curable composition of claim 1, characterized in that the composition is in the form of a waterborne liquid system.

18. The coating composition of claim 16, characterized in that the composition is in the form of a powder.

10 19. A coating composition based on the curable composition according to any one of claims 1-18.

15 20. A method of coating a substrate, comprising the steps of (A) applying to the substrate a coating composition then (B) curing the so applied coating composition to form a crosslinked film, characterized in that the coating composition is as set forth in claim 19.

20 21. A substrate coated with a crosslinked film derived from a coating composition, characterized in that the coating composition is as set forth in claim 19.

INTERNATIONAL SEARCH REPORT

International Application No

PC1/US 96/13831

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08K5/3492 C08L63/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,96 15185 (CYTEC) 23 May 1996 cited in the application see claims 1,2,16,17; example 1 ---	1
X	RESEARCH DISCLOSURE; no. 359, 1 March 1994, EMSWORTH, GB, pages 131-132, XP000440528 "ALKYLCARBAMYL METHYLATED AND BETA-HYDROXYALKYLCARBAMYL METHYLATED AMINOTRIAZINE CROSSLINKERS FOR POWDER COATINGS" see page 131, paragraph 4 & DATABASE WPI Week 9416 Derwent Publications Ltd., London, GB; AN 94-132843 see abstract --- -/--	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

4 December 1996

Date of mailing of the international search report

- 7. 01. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Engel, S

INTERNATIONAL SEARCH REPORT

Inter national Application No
PC1/US 96/13831

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 379 911 (PAREKH ET AL.) 12 April 1983 see column 2, paragraph 3 - paragraph 4 see examples I,IV-VI ---	1,4,5
A	DE,A,15 44 988 (J.R. GEIGY AG) 14 August 1969 see claims -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC1/US 96/13831

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9615185	23-05-96	NONE	
US-A-4379911	12-04-83	CA-A- 1155996	25-10-83
		EP-A- 0007682	06-02-80
		JP-C- 1574381	20-08-90
		JP-B- 2000383	08-01-90
		JP-A- 55018488	08-02-80
		US-A- 4404332	13-09-83
DE-A-1544988	14-08-69	CH-A- 450716	
		FR-A- 1451701	07-12-66
		GB-A- 1089500	
		NL-A- 6513788	26-04-67
		US-A- 3418392	24-12-68